

PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : D21H 21/16, 17/29, 17/17, 17/16	A1	(11) International Publication Number: WO 97/35068 (43) International Publication Date: 25 September 1997 (25.09.97)
(21) International Application Number: PCT/EP97/01308 (22) International Filing Date: 14 March 1997 (14.03.97) (30) Priority Data: 196 10 995.7 21 March 1996 (21.03.96) DE (71) Applicant (for all designated States except US): BETZDEAR-BORN INC. [US/US]; 4636 Somerton Road, Treviso, PA 19053-6783 (US). (72) Inventors; and (75) Inventors/Applicants (for US only): HASSLER, Thord, G., G. [SE/SE]; Stensogatan 46, S-253 72 Kydeback (SE). SCHUETZ, Jürgen, Friedrich [DE/DE]; Schmiedestrasse 15, D-24395 Gelting (DE). SMITH, Bryan, Cecil [GB/SE]; Kielergatan 28B, S-252 69 Raa (SE). (74) Agent: VON KAMEKE, Allard; Uexküll & Stolberg, Beselerstrasse 4, D-22607 Hamburg (DE).	(81) Designated States: AU, BR, CA, CN, JP, KR, NO, NZ, US, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>	
(54) Title: PAPER SIZE AND PAPER SIZING PROCESS (57) Abstract Disclosed are a paper size consisting essentially of a) alkyl ketene dimer and/or alkenyl succinic acid anhydride; b) degraded, liquid cationic starch having a cationic charge density of 0.5 to 3.5 meqv/g, a degree of substitution of more than 0.1 and a viscosity of less than 10000 cps (30 % by weight solution in water at 25 °C); and c) water, and a process for making paper products in which this paper size is added to the pulp. The invention allows the production of AKD and/or ASA sizes on-site in paper plants using simple mixing equipment.		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakhstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

Paper size and paper sizing process

The present invention relates to a paper size consisting essentially of an alkyl ketene dimer (AKD) and/or alkenyl succinic acid anhydride (ASA) sizing agent, a cationic starch emulsifier and water. Further the invention relates to a paper sizing process using a paper size which is essentially composed of an alkyl ketene dimer and/or alkenyl succinic acid anhydride sizing agent, a cationic starch emulsifier and water.

AKD and ASA sizes are widely used in the production of paper and cardboard. For good sizing efficiency it is required that the sizing agent is applied in the form of very small particles. Thus, AKD sizes are currently supplied to paper and cardboard manufacturers as fully formulated size dispersions or emulsions. However, such dispersions and emulsions have several disadvantages. For example, they often have to be transported over considerable distances to the paper plant which is uneconomical since such transport includes the transport of great amounts of water. Further, stability of AKD dispersions and emulsions is a problem. Accordingly such AKD size formulations include adjuvants like protective colloids, emulsifiers, surfactants etc. Such ingredients are not necessarily required for good sizing. To the contrary it is known that surfactants, particularly anionic surfactants, will not assist the deposition of AKD particles onto anionically charged fibers and will tend to reduce the performance of the sizing composition. Finally, during transport and storage the AKD may react with the aforementioned ingredients. Again this impairs the efficiency of the AKD size.

- 2 -

- To avoid these disadvantages of AKD dispersions and emulsions it has already been proposed in the past to prepare the AKD sizing composition directly at the place of application, namely the paper plant. However, the problem is that emulsifying AKD is not
5 easy and requires considerable know-how and expensive mixing equipment, namely high pressure homogenisers. It is not realistic and would be highly uneconomical to supply every paper plant with a high pressure homogeniser.
- 10 Therefore there have been several proposals in the past for economically feasible on-site processes for producing AKD and ASA sizes. However, it is not known that any of these proposals has gained commercial importance with regard to AKD sizes, while ASA sizes are mostly produced on-site.
- 15 DE-AS 25 33 411 includes a detailed discussion of the above outlined problems and discloses a process for sizing paper products using an aqueous emulsion containing AKD and an emulsifier selected from specific polyoxyalkylenealkyl or polyoxyalkylene-
20 alkylaryl ethers or corresponding mono- or diesters. It is reported that emulsification only requires stirring or passing the mixture through a mixing valve or an aspirator. It is even claimed that particularly selected mixtures can be used in sizing without a prior emulsification step.
- 25 Other proposals for on-site preparation of AKD and ASA sizes are disclosed in DE-OS 24 39 026, PCT-Application WO 94/13883, GB-A-2 252 984, EP-B-0 220 941 and EP-B-0 228 576.
- 30 It has now been surprisingly found that AKD and/or ASA sizes can be produced on-site at a paper plant in a simple manner by using a specific cationic starch emulsifier.

Thus the present invention relates to a paper size consisting
35 essentially of

- 3 -

- a) alkyl ketene dimer and/or alkenyl succinic acid anhydride,
- b) degraded, liquid cationic starch having a cationic charge density of 0.5 to 3.5 meqv/g, a degree of substitution of more than 0.1 and a viscosity of less than 10000 cps (30% by weight solution in water at 25°C), and
- 5 c) water.

Further the invention relates to a process for making paper products in which a paper size is added to the pulp which is
10 essentially composed of

- a) alkyl ketene dimer and/or alkenyl succinic acid anhydride,
- b) degraded, liquid cationic starch having a cationic charge density of 0.5 to 3.5 meqv/g, a degree of substitution of
15 more than 0.1 and a viscosity of less than 10000 cps (30% by weight solution in water at 25°C), and
- c) water.

Preferred embodiments of the present invention will become apparent from the following description and the claims.
20

Useful alkyl ketene dimers are those of the formula $(RCH=C=O)_2$ wherein R is selected from saturated or unsaturated alkyl radicals with at least eight carbon atoms, cycloalkyl radicals with
25 at least six carbon atoms, aryl radicals, aralkyl radicals and alkaryl radicals or mixtures thereof (compare the definition of alkyl ketene dimers useful in paper sizing in the prior art, e.g. DE-AS 25 33 411 and DE-AS 23 35 756). Convenient are liquid AKDs in which R includes a high proportion of unsaturated C_{16}
30 radicals (derived from oleic acid) or short chain alkyl radicals, particularly C_{12} - C_{14} radicals (derived from coconut fatty acids).

Useful alkenyl succinic acid anhydrides are those with a hydrocarbon radical having 7 to 30 and preferably 14 to 30 carbon
35

- 4 -

atoms. Further it is preferable that said hydrocarbon radical is a saturated linear chain or branched radical.

The cationic starch emulsifier useful in the present invention is distinguished over cationic starches used in the prior art for preparing AKD and ASA emulsions in that it is a degraded, liquid cationic starch having a cationic charge density of 0.5 to 3.5 meqv/g, a degree of substitution of more than 0.1 and a viscosity of less than 10000 cps. The term "liquid starch" is used to clearly distinguish the cationic starches useful in the present invention over conventional cationic starches and designates an aqueous cationic starch solution which in contrast to aqueous solutions of conventional cationic starches is liquid at a starch concentration of 30% by weight at room temperature or slightly above room temperature. Thus, the viscosity of the starch is determined for a 30% by weight solution in water at 25 °C using a Brookfield viscometer. It is important that the liquid starch has the stated viscosity at a concentration of 30% by weight since the concentration of the degraded, liquid cationic starch is around 30% by weight after preparation (see below). More preferred ranges for the degraded, liquid cationic starch are a cationic charge density of 1.0 to 2.0 meqv/g, a degree of substitution (D.S.) of more than 0.25 and preferably 0.4 to 1.0, and a viscosity of less than 5000 cps, e.g. 2500 to 3500 cps.

The cationic starches useful in the present invention are quaternary ammonium alkyl ethers made for example by reacting starch under alkaline conditions with 2,3-epoxypropyltrimethylammonium chloride. Such cationization of starches is well known in the art and for example disclosed in US-A-4 088 600, the disclosure of which is included herein by reference (see also US patents 2 876 217 and 4 840 705).

It is important that the starch is sufficiently degraded before, during or after cationization so that a liquid cationic starch exhibiting the required viscosity is obtained. Thus, the catio-

- 5 -

nization can be carried out with an already degraded starch. Such starch is commercially available. Alternatively cationization can be carried out with non-degraded starch and thereafter sufficient acid (e.g. hydrochloric acid) is added to reduce the pH to about 0.5 to 1.0. The cationized starch is thus hydrolyzed and degraded. Once the required viscosity is obtained the pH is returned to neutral with e.g. caustic soda. Depending on the reaction conditions some degrading of the starch also takes place during the cationization stage. Therefore it is important to control the viscosity of the final degraded, liquid cationic starch so that it is within the above described ranges.

Any starch type is acceptable for preparing emulsifiers useful in the present invention but waxy maize, maize and potato starches are preferred.

The charge density of the useful cationic starches is determined in accordance with known methods based on the titration with the anionic polyelectrolyte PVSK (polyvinyl sulphate, potassium salt). Such titration can be carried out using commercial apparatus like the PCD-Titrator of Müttek Laser und opto-elektronische Geräte GmbH, Germany.

The degree of substitution (D.S.) of the highly degraded liquid cationic starch is also determined by the above titration with PVSK and thus relates to the actual degree of substitution of the starch molecules, while the D.S. values stated in the prior art mostly relate to theoretical values based on the assumption of complete reaction of the cationising agent with the starch.

In accordance with the present invention AKD and cationic starch emulsifier are used in weight ratios (based on solids contents) of 10:1 to 1:1, preferably 6:1 to 2:1 and most preferably 5:1 to 3:1. Very good results are obtained at a ratio of 8:3.

- 6 -

The AKD concentration in the paper size according to the present invention can be up to 25% by weight, 10 to 20% by weight being preferred. The corresponding concentration of the cationic starch emulsifier depends on the desired particle size in the final paper size formulation, higher concentrations resulting in improved particle size distributions. For example at a level of 20% by weight of AKD the concentration of the cationic starch emulsifier (based on solids content) is preferably about 10% by weight.

10

As mentioned above good sizing efficiency requires very small particle sizes of the AKD dispersion or emulsion. Accordingly particle sizes of 0.1 to 20 μm are suitable, particle sizes of 0.3 to 10 μm (e.g. a particle size distribution having a maximum below 3 μm) being preferred. The particle size measurement is carried out by laser light scattering using a MasterSizer apparatus of Malvern Instruments Ltd (for details compare MasterSizer E, Instrument Manual, Manual No. MAN 0060, Issue 1.0, May 1992; applicants have used the standard OHD refractive index model, see particularly Section 4.4).

15
20

The paper size according to the present invention is used in conventional amounts which crucially depend on the type of paper or board being produced. Usually amounts of up to 1.5 mg AKD/g paper are sufficient. Some papers (e.g. those with precipitated calcium carbonate filler) require significantly higher dosages of AKD.

25

When using ASA also very small particle sizes are required and conventional amounts are used. Thus, the above requirements outlined for AKD also apply to ASA.

30

Of course, besides the above described components conventional additives like alum, retention aids, antifoams, pH control agents etc. can be included. However, these are not essential with regard to the present invention.

35

- 7 -

The preparation of the paper size according to the present invention can be carried out continuously or batch-wise and does not require the use of high pressure homogenization apparatus. Thus custom built emulsification units can be used which are
5 easy to handle and comparatively inexpensive. In case solid AKD is used, it is preferred that it is in the form of fine particles, e.g. flakes, prills, powder etc. First the cationic starch is mixed with water and the mixture is then heated to a suitable temperature (e.g. 60°C). The AKD melt is then added to the
10 starch solution under stirring with some kind of higher speed mixer (such as an Ultra Turrax). Stirring is continued until a homogeneous emulsion is obtained. When liquid AKD and/or ASA is used, mixing with the starch solution can take place at room temperature.

15 The cationic starch emulsifier useful in the present invention not only allows on-site preparation of AKD paper size, but also simplifies on-site preparation of ASA paper size since it avoids the laborious on-site preparation of starch emulsifier based on
20 conventional cationic starches. Further it is an advantage of the present invention that components which are all liquid can be used which facilitates handling and dosing. In addition liquid AKD and ASA are fully mixable so that they can be used in any desirable ratio. By using mixtures of AKD and ASA it is
25 possible to make use of the advantages of these sizing agents but suppress or even eliminate their individual disadvantages. For example ASA usually provides a better particle size distribution than AKD. However, by including about 25% by weight ASA, based on the combined weight of AKD and ASA, a particle size
30 distribution is achievable which is already quite similar to said obtained by using ASA alone. In case a mixture of AKD and ASA in a weight ratio of 1:1 is used, the achievable particle size distribution is practically identical with said obtainable by using ASA alone.

- 8 -

The formulations according to the present invention can be used alone or in combination with other sizing agents, e.g. emulsions or dispersions comprising AKD, ASA, rosin, isocyanates or other known sizing agents. Rosin sizes can be made using any known rosin, e.g. anionic rosin, cationic rosin, rosin soaps, fortified rosin and rosin esters or blends of these. The other sizing agents can be added to the pulp before, after or simultaneously with the sizing agent according to the present invention. They may also be pre-blended with the sizing agent of the present invention before addition to the pulp. Alternatively the other sizing agent can be added during the emulsification step when preparing the sizing agent of the present invention.

15

Example 1

The following formulations (% by weight) were prepared:

	(a)	(b)	(b*)	(c)	(e)	(f)
Stearic AKD	20%					
Oleic AKD		20%	10%			10%
Coco AKD				20%		
ASA					20%	10%
Cat. starch (based on solids content)	5%	5%	2.5%	5%	5%	5%
Water	75%	75%	87.5%	75%	75%	75%

The cationic starch was a highly degraded, liquid cationic starch with a charge density of 1.32 meqv/g, a D.S. of 0.48 and a viscosity of 3500 cps at a concentration of 36.4% by weight.

In (a) the stearic AKD was broken into small pieces and then melted. The cationic starch was mixed with water and heated to about 60°C. The stearic AKD melt was then added to the starch

- 9 -

solution and the mixture was emulsified for 30 seconds at 13.500 rpm in an Ultra Turrax.

In (b), (b*), (e) and (f) the oleic AKD and ASA were liquids and mixing took place as for (a) but at room temperature.

In (c) coco (C_{12} - C_{18}) AKD was heated slightly to melt it and then emulsified at room temperature as in (a).

10 All six samples were then used in identical sizing experiments. Hydrocol (cationic polyacrylamide and bentonite) was used as a retention aid. No fillers were used in these experiments. A standard commercial product (d) comprising (C_{16} - C_{18}) AKD, cationic starch having a D.S. of 0.08, an anionic additive and a small
15 amount of alum, which is produced by high pressure homogenisation of AKD, starch and anionic additive in water using e.g. a Gaulin type homogeniser, was tested at the same dosage and under the same conditions for comparison.

20 At an AKD and/or ASA dosage of about 1.5 g per kg fibres in the pulp the following results were obtained.

	Cobb 60 (g/m^2)
a)	21.7, 19.9
25 b)	20.8, 22.3
c)	19.6, 20.5
d)	22.2, 22.1
e)	22.4, 19.5
f)	20.7, 20.5

30 Cobb 60 relates to the amount of water taken up by a unit area of paper in one minute. The lower the value, the better the sizing. Values of 25 or less indicate satisfactory sizing efficiency.

- 10 -

It can be seen that the sizing with the simple emulsions according to the present invention is as good or better than the standard commercial AKD size.

5 Example 2

Formulations (a), (b*), (e) and (f) as well as standard commercial product (d) were also used in a sizing experiment to make paper containing about 15% by weight chalk filler. Results were
10 as follows.

	Dosage (g/kg fibres)	Cobb 60 (g/m ²)
a)	1.5	17.6, 17.3
b*)	1.5	18.6
15 d)	1.6	20.4
e)	1.5	20.5, 23.3
f)	1.5	20.9, 21.0

These results confirm that the AKD and/or ASA emulsions of the
20 present invention give sizing as good as or better than the standard commercial product at a dosage of 1.5 g/kg fibre in the pulp.

As demonstrated by the above examples the present invention
25 allows simple on-site preparation of AKD and/or ASA size at a paper plant, avoids the disadvantages of fully formulated emulsions, particularly the adverse effects of surfactants included in such fully formulated emulsions, and combines the advantageous properties of cationic starch, i.e. the cationic starch
30 serves as an emulsifier and at the same time aids retention. Particularly convenient is the preferred embodiment of the present invention in which only liquid components are used for size preparation. This allows easy handling and exact dosing with minimum apparatus requirements.

- 11 -

Claims

1. Paper size consisting essentially of
 - a) alkyl ketene dimer and/or alkenyl succinic acid anhydride,
 - b) degraded, liquid cationic starch having a cationic charge density of 0.5 to 3.5 meqv/g, a degree of substitution of more than 0.1 and a viscosity of less than 10000 cps (30% by weight solution in water at 25°C), and
 - c) water.
2. Paper size according to claim 1 in which the degraded, liquid cationic starch has a cationic charge density of 1.0 to 2.0.
3. Paper size according to claim 1 or 2 in which the degraded, liquid cationic starch has a degree of substitution of more than 0.25, preferably 0.4 to 1.0.
4. Paper size according to anyone of claims 1 to 3 in which the degraded, liquid cationic starch has a viscosity of less than 5000 cps, preferably in the range of 2500 to 3500 cps.
5. Paper size according to anyone of claims 1 to 4 in which the alkyl ketene dimer is liquid.
6. Process for making paper products in which a paper size is added to the pulp which is essentially composed of
 - a) alkyl ketene dimer and/or alkenyl succinic acid anhydride,
 - b) degraded, liquid cationic starch having a cationic charge density of 0.5 to 3.5 meqv/g, a degree of substitution of more than 0.1 and a viscosity of less than 10000 cps (30% by weight solution in water at 25°C), and
 - c) water.

- 12 -

7. Process according to claim 6 in which degraded, liquid cationic starch is used having a cationic charge density of 1.0 to 2.0 meqv/g.
8. Process according to claim 6 or 7 in which degraded, liquid cationic starch is used having a degree of substitution of more than 0.25, preferably 0.4 to 1.0.
9. Process according to anyone of claims 6 to 8 in which degraded, liquid cationic starch is used having a viscosity of less than 5000 cps, preferably in the range of 2500 to 3500 cps.
10. Process according to anyone of claims 6 to 9 in which liquid alkyl ketene dimer is used.
11. Process according to anyone of claims 6 to 10 in which before, after or simultaneously with the addition of the paper size also other sizing agents are added to the pulp.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 97/01308

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 D21H21/16 D21H17/29 D21H17/17 D21H17/16

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 D21H

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 93 10305 A (RAISION TEHTAAT OY AB) 27 May 1993 see claims 1,3 ---	1,2,6,7
Y	US 5 178 730 A (BIXLER HARRIS J ET AL) 12 January 1993 see claims 1,10 ---	1-11
Y	PATENT ABSTRACTS OF JAPAN vol. 017, no. 100 (C-1030), 26 February 1993 & JP 04 289295 A (KAO CORP), 14 October 1992, see abstract --- -/-	1,10

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- *&* document member of the same patent family

Date of the actual completion of the international search 25 July 1997	Date of mailing of the international search report 11.08.97
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+ 31-70) 340-3016	Authorized officer Philosoph, L

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 97/01308

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	<p>DATABASE WPI Section Ch, Week 8401 Derwent Publications Ltd., London, GB; Class A97, AN 84-002320 XP002036146 & JP 58 197 397 A (NICHIDEN KAGAKU KK) , 17 November 1983 see abstract</p> <p>---</p>	1,3-6, 8-11
Y	<p>DATABASE WPI Section Ch, Week 9305 Derwent Publications Ltd., London, GB; Class A11, AN 93-039372 XP002036147 & JP 04 363 301 A (NICHIDEN KAGAKU KK) , 16 December 1992 see abstract</p> <p>-----</p>	1,3-6, 8-11

INTERNATIONAL SEARCH REPORT

information on patent family members

Inter nal Application No

PCT/EP 97/01308

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9310305 A	27-05-93	FI 915310 A EP 0626022 A US 5578169 A	12-05-93 30-11-94 26-11-96
US 5178730 A	12-01-93	EP 0610217 A WO 9325754 A	17-08-94 23-12-93